



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 17/06, 3/10, 3/06, 1/22, 11/04	A1	(11) International Publication Number: WO 98/20104 (43) International Publication Date: 14 May 1998 (14.05.98)
(21) International Application Number: PCT/US97/19165 (22) International Filing Date: 30 October 1997 (30.10.97) (30) Priority Data: 60/030,610 6 November 1996 (06.11.96) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors: ADAMS, Donald, Scott; 4705 Heger Drive, Cincinnati, OH 45217 (US). PALLARES-GALVAN, Francisco; Real de Abedules 9-A, Colonia Real de Atizapan, Lopez Mateos, México 52945 (MX). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: BR, CN, MX, TR. Published <i>With international search report.</i>
(54) Title: NEUTRALIZATION PROCESS FOR MAKING AGGLOMERATE DETERGENT GRANULES (57) Abstract The subject invention involves a continuous process for producing agglomerate detergent granules comprising the following steps: (a) grinding carbonate selected from sodium carbonate, potassium carbonate, and mixtures thereof, to a freshly ground particulate carbonate having a median particle size of from about 2 to about 50 microns, (b) preparing a mixture in a high-speed mixer by feeding to the mixer raw materials consisting essentially of the following: (1) from about 10 % to about 25 % an alkylbenzene sulfonic acid; (2) from about 25 % to about 60 % the freshly ground particulate carbonate, the amount of carbonate being at least about 10 times the amount theoretically needed to neutralize the alkylbenzene sulfonic acid; (3) from about 5 % to about 40 % a phosphate builder selected from polyphosphates, pyrophosphates, and mixtures thereof; (4) from about 5 % to about 50 % a sodium sulfate; (5) from 0 % to about 10 % other surfactants; (6) from 0 % to about 9 % water (including water in the raw materials); and (7) from 0 % to about 10 % other materials; (c) agglomerating the mixture from step (a) in a moderate-speed mixer; whereby the alkylbenzene sulfonic acid is neutralized by the carbonate and the agglomerate detergent granules are produced, and wherein the granules produced are substantially free of flow aids selected from silicas, clays, diatomaceous earth, aluminosilicates, perlite, calcite, and mixtures thereof.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

NEUTRALIZATION PROCESS FOR MAKING AGGLOMERATE DETERGENT GRANULES

TECHNICAL FIELD

The subject invention involves a process for making agglomerate detergent granules by neutralizing anionic surfactant acid in a high-speed mixer.

BACKGROUND OF THE INVENTION

Detergent granules containing anionic surfactant are typically produced by neutralizing the acid form of the surfactant in the presence of a detergent builder. Low density granules are commonly produced by making an aqueous paste of the neutralized surfactant and builder, and spray drying the paste to form granules. Higher density detergent granules have been made using agglomeration and particle formation in high speed mixers, without the need for spray drying. One type of high density agglomerate detergent granules are made by carrying out the surfactant neutralization and incorporating a builder in a high-speed mixer. Typically, a flow aid is used to obtain desired agglomerate granule formation and flow in such a mixing process. A typical flow aid is zeolite or silica. Such flow aids are generally insoluble and can be captured in the fabric of the laundry after the washing process.

It is an object of the subject invention to provide a process for making agglomerate detergent granules in a high-speed mixer by neutralizing anionic surfactant acid with alkali metal carbonate.

It is a further object of the subject invention to provide such process where incorporation of a flow aid in the process is unnecessary and is avoided.

It is also an object of the subject invention to optionally feed an aqueous paste of another surfactant to such process.

SUMMARY OF THE INVENTION

The subject invention involves a process, preferably a continuous process, for producing agglomerate detergent granules comprising the following steps:

- (a) grinding carbonate selected from sodium carbonate, potassium carbonate, and mixtures thereof, to a freshly ground particulate carbonate having a median particle size of from about 2 to about 50 microns, preferably about 2 to about 20 microns,
- (b) preparing a mixture in a high-speed mixer by feeding to the mixer raw materials consisting essentially of the following:
 - (1) from about 10% to about 25% an alkylbenzene sulfonic acid;
 - (2) from about 25% to about 60% the freshly ground particulate carbonate, the amount of carbonate being at least about 10 times the amount theoretically needed to neutralize the alkylbenzene sulfonic acid;

- (3) from about 5% to about 40% a phosphate builder selected from polyphosphates, pyrophosphates, and mixtures thereof;
 - (4) from about 5% to about 50% a sodium sulfate;
 - (5) from 0% to about 10% other surfactants;
 - (6) from 0% to about 9% water (including water in the raw materials); and
 - (7) from 0% to about 10% other materials;
- (c) agglomerating the mixture from step (a) in a moderate-speed mixer, whereby the alkylbenzene sulfonic acid is neutralized by the carbonate and the agglomerate detergent granules are produced, and

wherein the granules produced are substantially free of flow aids selected from silicas, clays, diatomaceous earth, aluminosilicates, perlite, calcite, and mixtures thereof.

The subject invention also involves agglomerate detergent granules made by such a process.

DETAILED DESCRIPTION OF THE INVENTION

The subject invention involves a continuous two-step mixing process for producing agglomerate detergent granules by dry neutralizing alkylbenzene sulfonic acid with a freshly ground particulate alkali metal carbonate compound in the presence of a phosphate builder and sodium sulfate. Typically, such agglomerate detergent granules are then blended with other ingredients to produce a granular detergent product, especially those suitable for cleaning clothes.

All percentages herein are weight percent unless specified otherwise.

Raw Materials

Alkylbenzene Sulfonic Acid

A subject invention process involves neutralization of alkylbenzene sulfonic acid. The alkylbenzene sulfonic acid raw material preferably has a moisture content of less than about 0.3%, more preferably less than about 0.1%. Based on the total weight of raw materials fed to a subject process, the amount of alkylbenzene sulfonic acid is from about 10% to about 25%, preferably from about 17% to about 22%, also preferably from about 13% to about 18%.

Alkylbenzene sulfonic acid useful in a subject process includes that with an alkyl portion which is linear or branched, preferably having an average of from about 10 to about 16 carbon atoms, more preferably from about 11 to about 14 carbon atoms. Alkylbenzene sulfonic acid which includes branched alkyl is termed HABS (ABS when neutralized). Alkylbenzene sulfonic acid which is all linear is preferred because it is more easily biodegraded; it is termed HLAS (LAS when neutralized).

Carbonate

A subject invention process utilizes particulate alkali metal carbonate raw material, preferably consisting essentially of sodium carbonate, potassium carbonate, and mixtures thereof, for neutralization of the anionic surfactant acids. Sodium carbonate is preferred.

Alkali metal carbonate is fed to the subject process as powder having a median particle size of from about 2 microns to about 50 microns, preferably about 2 to about 20 microns, more preferably from about 5 microns to about 15 microns, and even more preferably from about 8 microns to about 12 microns. Alkali metal carbonate raw material preferably has a moisture content of less than about 2%, more preferably less than about 1%. Based on the total weight of raw materials fed to a subject process, the amount of alkali metal carbonate is from about 25% to about 60%, preferably from about 30% to about 55%, more preferably from about 35% to about 50%.

The alkali metal carbonate raw material as specified above, which is fed to a subject process, is freshly ground as described hereinafter. When ground to the fine particle size required for a subject process, alkali metal carbonate particles tend to absorb moisture from the surrounding atmosphere. This is believed to result from the substantial increase in particle surface area, and in the greater intimacy and packing of the ground particles. Under conditions where alkali metal carbonate can form hydrates, the finely ground carbonate will start caking and forming hard lumps, and will not have desired flow characteristics in the subject process. The lumping of the ground carbonate increases with moisture uptake by, and hydration of, the carbonate. At a moisture content of about 3%, for example, the ground carbonate becomes too lumpy and hardened to process adequately. Therefore, as used herein, "freshly ground carbonate" is free flowing, substantially free of lumps of carbonate, and has a moisture content of less than about 3%, preferably less than about 2%, and more preferably less than about 1%.

To neutralize the anionic surfactant acid, each carbonate ion (CO_3^{2-}) reacts with two acidic hydrogens (H^+). From this reaction, the amount of carbonate raw material needed to theoretically neutralize all the acid raw material can be determined. The amount of carbonate fed to a subject process is at least about 10 times that theoretically needed to neutralize the acid, preferably from about 11 times to about 20 times, more preferably from about 12 times to about 18 times, more preferably still from about 13 times to about 17 times.

Phosphate Builder

Phosphate builder raw material useful in a subject invention process is in particulate form and consists essentially of the water-soluble salts of polyphosphates or pyrophosphates or mixtures thereof. The phosphate builder raw material preferably has a moisture content of less than about 2%, more preferably less than about 1%. Based on the total weight of raw materials fed to a subject process, the amount of phosphate builder is from about 5% to about 40%, preferably from about 9% to about 19%, also preferably from about 16% to about 30%. Phosphate builder raw material is preferably obtained in powder form having a median particle size of from about 10 microns to about 50 microns, more preferably from about 20 microns to about 30 microns. If coarser raw material is obtained, a conventional pregrinding step can be used to obtain a desired particle size distribution.

A preferred phosphate builder useful in a subject process is sodium tripolyphosphate (STPP); STPP can be obtained commercially from, for example, FMC Corp. Another preferred phosphate builder is tetrasodium pyrophosphate (TSPP); TSPP can be obtained commercially from, for example, FMC Corp.

Sulfate

A subject invention process utilizes particulate sodium sulfate raw material. Sodium sulfate raw material preferably has a moisture content of less than about 2%, more preferably less than about 1%. Based on the total weight of raw materials fed to a subject process, the amount of sodium sulfate is from about 5% to about 50%, preferably from about 12% to about 30%. Sodium sulfate raw material is preferably obtained in powder form having a median particle size of from about 50 microns to about 200 microns, more preferably from about 100 microns to about 150 microns. If coarser raw material is obtained, a conventional pregrinding step can be used to obtain a desired particle size distribution.

Other Surfactants

Surfactants other than alkylbenzene sulfonic acid can be fed as raw materials to a subject process. Surfactants commonly used in detergent products include anionic, nonionic, cationic, zwitterionic, and amphoteric surfactants; typical listings of classes and species of such surfactants appear, for example, in U.S. Patent Nos. 3,664,961; 3,929,678; 4,844,821; 5,174,927; and 5,415,814, all incorporated herein by reference.

Such other surfactants may include anionic surfactants, such as alkyl ethoxy ether sulfate surfactant (AES), wherein the alkyl has an average of from about 10 to about 16 carbon atoms, preferably from about 12 to about 15 carbon atoms, and a degree of ethoxylation of from about 0.5 to about 9, preferably from about 2 to about 5, especially about 3; C₁₂-C₁₈ alkyl sulfates; and C₁₀-C₁₈ alkyl alkoxy carboxylates. Such other surfactants include cationic surfactants including quaternary ammonium surfactants, such as hydroxyalkyl quaternary

ammonium surfactant (HAQA) having 1 or 2, preferably 1, alkyl having an average of from about 10 to about 16, preferably from about 12 to about 14, carbon atoms; 1 or 2, preferably 2, alkyl having from 1 to about 3, preferably 1, carbon atoms; and 1 or 2, preferably 1, hydroxyethyl or hydroxypropyl, preferably hydroxyethyl, attached to the nitrogen, and a water soluble anion, preferably chloride. Such other surfactants may include nonionic surfactants, such as C₁₁-C₁₆ alkyl ethoxy alcohol surfactant, C₁₁-C₁₆ glycerol ether surfactant, C₁₁-C₁₆ alkyl polyglycoside and corresponding sulfated polyglycoside surfactants, C₁₂-C₁₈ α -sulfonated fatty acid ester surfactant, C₁₁-C₁₆ N-alkyl polyhydroxy fatty acid amide surfactant, and C₁₀-C₁₈ amine oxide surfactant. Such other surfactants may include zwitterionic and amphoteric surfactants, such as C₁₂-C₁₈ betaine and sulfobetaine surfactants. Preferably no more than one said other surfactant is fed to a subject process.

Typically, such other surfactants are fed to a subject process in the form of an aqueous paste comprising from about 30% to about 80%, preferably from about 40% to about 70%, said surfactant, the remainder (other than a minor amount (<1%) of impurities) being water. AES surfactant paste preferably comprises from about 50% to about 80% surfactant. HAQA surfactant paste preferably comprises from about 30% to about 50% surfactant. Even with the extra moisture added to the process with such aqueous paste of surfactant, the materials flow readily through the process steps and the agglomerate granules produced are free flowing.

Granules produced by a subject invention process optionally include from 0% to about 10% said other surfactants, preferably from about 1% to about 4%, also preferably from about 3% to about 7%.

Water

In a subject invention process, substantially the only water present in the materials as they go through the process is the water present in the raw materials and the water generated by the neutralization reaction. Throughout the process, the amount of total water in the materials being processed, including all water in the raw materials fed to the process, is preferably from 0% to about 9%, more preferably from about 1% to about 4%, also preferably from about 2% to about 6%, also preferably from about 3% to about 7%. The water loss (which is due to evaporation) during the subject process, based on the weight of the granules produced, is typically less than about 2%, preferably from about 0.5% to about 1.5%. The amount of moisture in detergent granules produced by the subject process is from 0% to about 7%, preferably from about 0.5% to about 5%, more preferably from about 1% to about 4%. The detergent granules thus produced may be somewhat hygroscopic and pick up moisture from the atmosphere.

Other Materials

Other optional materials which may be fed to a subject invention process include, but are not limited to, chelating agent, polymeric dispersing agent, polymeric soil release agent, dye transfer inhibiting ingredient, photobleach material, perfume, colorant, other minors, and raw material impurities.

Granules produced by a subject invention process comprise from 0% to about 10% of such other materials, preferably from 0% to about 4%, more preferably from 0% to about 2%.

Agglomerate detergent granules produced by a subject invention process optionally comprise chelating agent which may include amino carboxylate such as ethylenediamine tetraacetate and diethylenetriamine pentaacetate, amino phosphonate such as diethylenetriamine penta(methylene phosphonate); polymeric dispersing agent which may include polymeric polycarboxylate such as polymers of acrylic acid and copolymers of acrylic acid and maleic acid (or maleic anhydride), polyethylene glycol (preferably having a molecular weight of from about 1500 to about 10,000), carboxymethylcellulose material, and alkoxylated polyalkyleneamine material; polymeric soil release agent which may include cellulosic derivatives, and such agents disclosed in U.S. Patent Nos. 5,415,807 issued to Gosselink et al. on May 16, 1995. A preferred soil release agent is described in Example V of U.S. 5,415,807 (incorporated herein by reference), columns 19-20; it is a doubly end-capped ester made from sodium 2-(2-hydroxyethoxy)-ethanesulfonate, dimethyl terephthalate, dimethyl 5-sulfoisophthalate sodium salt, ethylene glycol and propylene glycol, with 12% linear dodecylbenzene sulfonate as a stabilizer (hereinafter SRA).

Agglomerate detergent granules produced by a subject invention process optionally comprise photobleach such as zinc phthalocyanine sulfonate available as QUANTUM® from Ciba Geigy; optical brightener or whitening agent, such as 4,4'-bis((4-anilino-6-bis(2-hydroxyethyl)amino-1,3,5-triazin-2-yl)amino)stilbene-2,2'-disulfonic acid disodium salt, 4,4'-bis(2-sulfostyryl)biphenyl, 4,4'-bis((4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino)-stilbene-2,2'-disulfonic acid disodium salt, PHORWHITE® from Verona, TINOPAL® from Ciba Geigy, and ARTIC WHITE® from Hilton Davis; enzymes such as protease, amylase, lipase, cellulase, and peroxidase; bleaching agent such as perborate bleach, and bleach activator such as nonanoyloxybenzene sulfonate (NOBS) or tetraacetyl ethyleendiamine (TAED).

Agglomerate detergent granules produced by a subject invention process optionally comprise miscellaneous ingredients, such as colorant, germicide, perfume, and other minors, some of which are impurities carried in with other raw materials.

Agglomerate detergent granules made by a process of the subject invention preferably have a bulk density of greater than about 550 g/l, more preferably from about 600 g/l to about 900 g/l, more preferably still from about 650 g/l to about 860 g/l, still more preferably from about 700

g/l to about 830 g/l. Agglomerate detergent granules from a process of the subject invention preferably have an average particle size of from about 200 microns to about 600 microns, more preferably from about 300 microns to about 500 microns, more preferably still from about 350 microns to about 450 microns.

In a subject invention process, the materials being processed and the agglomerate detergent granules produced are maintained substantially free of flow aids such as silicas, clays, diatomaceous earth, aluminosilicates (zeolites), perlite, and calcite (calcium carbonate) and mixtures thereof. As used herein, "substantially free of flow aids" means that the agglomerate granules contain less than about 2% of flow aids, preferably less than about 1%, more preferably less than about 0.5%, and most preferably 0%.

Process Steps

Commercially available carbonate typically has a median particle size of about 50-150 microns, and contains less than 2%, preferably less than 1% moisture. As a preliminary step to a subject continuous agglomerate-making process, such carbonate is ground to the particle size specifications defined herein before using any suitable grinder capable of producing such finely ground carbonate. A preferred grinder used for this purpose is an air-classifier mill, such as the Mikro-ACM CX Model 300 available from Hosokawa Micron Powder Systems, Summit, New Jersey.

The particle size distribution of the ground carbonate is determined by any instrument which approximates such particle size as the diameter of a spherical particle occupying the same volume as the particle being measured. The median particle size is that size which has 50% of the particles being smaller and 50% larger. A suitable instrument for measuring the particle size of the ground carbonate is the Malvern Series 2600 Optical Laser, available from Malvern Instrument Company, Malvern, Pennsylvania.

Alkali metal carbonates form a stable monohydrate at temperatures below the hydration temperature (the temperature below which the carbonate will form a hydrate from moisture, and above which the carbonate can liberate bound water of hydration). For sodium carbonate, the hydration temperature is about 50°C. Carbonate fed to a subject continuous process is "freshly ground", having been ground preferably less than about 48 hours prior to being fed to a subject process, more preferably less than about 24 hours prior, more preferably still less than about 12 hours prior, still more preferably less than about 8 hours prior. Alternatively, "freshly ground" carbonate can be stored up to about four weeks, preferably up to about two weeks, more preferably up to about one week, after grinding, in a storage container which minimizes, and preferably prevents, hydration of the ground carbonate. Preferred is a storage container which substantially seals off the ground carbonate from atmospheric or other moisture sources. Also

preferred is a storage container which maintains the temperature of the ground carbonate at a temperature above the hydration temperature (for sodium carbonate about 50°C).

A preferred continuous process of the subject invention comprises two mixing steps; said process preferably consists essentially of the two steps, more preferably consists of the two steps. The first step of such a process is carried out in a high-speed, high-shear mixer. Suitable mixers for this step include, for example, the Loedige CB®, the Shugi Granulator®, and the Drais K-TTP®. A preferred mixer for the first step of a subject invention process is the Loedige CB®. Typically, the high-speed mixer has a substantially cylindrical mixing chamber which is from about 0.3m to about 1m in diameter and from about 1m to about 3.5m in length. For a mixer used in the first step of a subject invention process, a preferred mixer has a central shaft, with mixer blades attached, which preferably rotates at a speed of from about 200 rpm to about 1800 rpm, more preferably from about 225 rpm to about 1250 rpm, more preferably still from about 250 rpm to about 600 rpm, the speed generally being lower for larger mixers. The high-speed mixer preferably is water-jacketed to permit cooling water to flow through the mixer jacket, in order to remove heat generated by the neutralization reaction.

For the first step of the process, the above raw materials are typically fed to the high-speed mixer near one end of the cylindrical chamber and intimately mixed as they proceed through the chamber; the mixture is discharged near the other end of the cylindrical chamber. The typical average throughput rate is from about 0.2 kg/sec to about 17 kg/sec, especially from about 9 kg/sec to about 13 kg/sec, the higher throughput rates generally being achieved using larger mixers. The average residence time of materials in the first-step mixer is preferably from about 2 seconds to about 30 seconds, more preferably from about 5 seconds to about 20 seconds, more preferably still from about 10 seconds to about 15 seconds.

Cooling water at a temperature of from about 5°C to about 25°C is preferably fed to the water jacket of the high-speed mixer. The temperature of the mixture at the discharge from the high-speed mixer is typically from about 35°C to about 70°C, preferably from about 45°C to about 55°C.

Much of the neutralization of the alkylbenzene sulfonic acid by the carbonate occurs in the first step of a subject invention process. Preferably, substantially all of the neutralization takes place in the first step. The neutralization reaction may be completed after the mixture discharges from the first-step mixer. The alkylbenzene sulfonic acid is substantially completely neutralized, preferably completely neutralized, during a subject invention process.

The materials discharged from the first-step mixer are typically fed substantially immediately into the second-step mixer. The average residence time for materials between the mixers is preferably less than about 5 minutes, more preferably less than about 1 minute.

The second step of a process of the subject invention is carried out in a moderate-speed mixer. Suitable mixers for this step include plowshare mixers, for example, the Loedige KM® and the Drais K-T®. The Loedige KM® is the preferred mixer for the second step of a subject invention process. Typically, the moderate-speed mixer has a substantially cylindrical mixing chamber which is from about 0.6m to about 2m in diameter and from about 2m to about 5m in length. A preferred mixer has a central shaft, with mixer blades attached, which preferably rotates at a speed of from about 40 rpm to about 160 rpm, more preferably from about 45 rpm to about 140 rpm, more preferably still from about 50 rpm to about 80 rpm, the speed generally being lower for larger mixers. The moderate-speed mixer preferably is water-jacketed to permit warm water to flow through the mixer jacket, in order to maintain the temperature of product in the moderate-speed mixer at about its incoming temperature.

For the second step of a subject process, the mixture of materials discharged from the first-step mixer is typically fed to the moderate-speed mixer near one end of the cylindrical chamber, mixed as it proceeds through the chamber, and discharged near the other end of the cylindrical chamber. Agglomerate granules having good uniformity are achieved in the moderate-speed mixer. Typically, the throughput rate for the second step is the same as for the first step. The average residence time of the materials in the second-step mixer is preferably from about 20 seconds to about 300 seconds, more preferably from about 30 seconds to about 90 seconds, more preferably still from about 40 seconds to about 55 seconds.

Water at a temperature of from about 20°C to about 50°C is preferably fed to the water jacket of the moderate-speed mixer. The temperature of the mixture at the discharge of the moderate-speed mixer is typically from about 35°C to about 70°C, preferably from about 45°C to about 55°C.

EXAMPLES

The following non-limiting examples exemplify processes of the subject invention.

The following raw materials are used in Examples 1-3:

- | | |
|------------|------------------------------------------------------------------------------------------------------------------------------|
| HLAS: | linear C ₁₁ -C ₁₃ alkylbenzene sulfonic acid (96.5% active). |
| Carbonate: | sodium carbonate, from Industrias del Alkali. |
| STPP: | sodium tripolyphosphate, from Quimie Commercial. |
| Sulfate: | sodium sulfate, from Quimica del Ray. |
| HDQA: | linear C ₁₂ -C ₁₄ alkyl dimethyl hydroxyethyl quaternary ammonium chloride, from Hoechst (40% active). |
| AES: | linear C ₁₂ -C ₁₅ alkyl ethoxy (3) ether sulfate, from Hickson-Manro (70% active). |
| ZPS: | zinc phthalocyanine sulfonate, tradename QUANTUM®, from Ciba-Geigy (8% active). |

Examples 1-3

Commercial grade sodium carbonate having a median particles size of about 100 microns and a moisture content of less than 1% is ground at a rate of 7500 kg/hr using a Hosakawa Mikro-ACM CX Model 300 air-classifier mill. For Examples 1-3, two-grinders are used in parallel to double this throughput rate. The resulting freshly ground carbonate, having a median particle size of 10 microns and a moisture content of less than 1%, is fed to the Loedige CB-100® mixer within 8 hours of being ground.

Examples 1-3 are carried out using a water-jacketed Loedige CB-100® as the high-speed mixer and a water-jacketed Loedige KM-15000® mixer as the moderate-speed mixer. Product passes immediately from the high-speed mixer into the moderate-speed mixer. Table 1 shows the production rate for each of Examples 1-3, and indicates the mixer speed and water-jacket temperature for each mixer. Table 1 also shows the amount of the above freshly ground carbonate fed to the mixer in terms of the multiple of that amount needed to neutralize all of the anionic surfactant acids fed to the process for each example.

Table 1

	Example		
Process Variable	1	2	3
Production Rate (kg/sec)	8.3	8.3	8.3
CB-100			
Mixer speed (rpm)	225-325	225-325	225-325
Jacket temp. (°C)	7	7	7
KM-15000			
Mixer speed (rpm)	50-60	50-60	50-60
Jacket temp (°C)	21	21	21
Amount of carbonate (times that needed to neutralize acids)	16	15	14

In Examples 1-3, raw materials are fed continuously to the high-speed mixer. The rate in kg/hr at which each raw material is fed to the high-speed mixer in each of Examples 1-3 is shown in Table 2.

Table 2

Raw Material	Example		
	1	2	3
HLAS	5,790	4,340	6,250
Carbonate	14,200	10,960	14,200
STPP	3,215	6,915	5,340
Sulfate	5,890	5,920	4,620
HDQA (40% aqueous paste)	1,275	--	--
AES (70% aqueous paste)	--	2,140	--
ZPS	3.2	3.2	3.2

The agglomerate detergent granules produced in Examples 1-3 have the compositions percentages shown in Table 3.

Table 3

Product Component	1	2	3
NaLas	20.0	15.0	21.6
Na carbonate	44.0	34.0	43.7
STPP	10.7	23.1	17.8
Na sulfate	20.0	20.0	15.4
Moisture	3.0	2.7	0.8
HDQA	1.7	--	--
Na AES	--	5.0	--
ZPS	0.00085	0.00085	0.00085
Misc.	0.6	0.2	0.7
Product density (g/l)	750	750	820

Finished Detergent Product

Agglomerate detergent granules made by a process of the subject invention may be used as a finished detergent product, but typically it is combined with other materials to form such a finished product. The following exemplifies the making of such a finished laundry detergent product suitable for use in an automatic washer.

Example 4

The following is a list of raw materials, in addition to those listed above, utilized to make spray-dried detergent granules to be mixed with agglomerate detergent granules from a subject process.

- Silicate: sodium silicate with ratio of $\text{SiO}_2/\text{Na}_2\text{O} = 1.6$, from Vitro PQ (45% solids).
- A/M copolymer: copolymer of acrylic acid and maleic acid, tradename SOKOLAN HP-22® from BASF (40% active).
- CMC: carboxymethylcellulose, from Amtex (70% active).
- DTPA: diethylenetriamine pentaacetate, sodium salt, tradename CHEL DTPA 41® from Ciba Geigy (40% active).
- Brightener: 4,4'-bis(2-sulfostyryl)biphenyl, tradename TINOPAL CBS® from Ciba Geigy (33% active).

Spray-dried granules are made from the following raw materials and amounts:

Material	Amount (kg)
Heel	1850
HLAS	647
Silicate	847
Water	1239
A/M copolymer	70
CMC	16.6
DTPA	44
HDQA	73
ZPS	5.9
Brightener	7
Sulfate	1846
STPP	795

At the start of the process, the crutcher contains a heel from the previous batch made therein which is the same composition as this example; it is heated to about 65°-70°C using the crutcher steam jacket, if needed. The HLAS, silicate, water, A/M copolymer, CMC, DTPA, HDQA, and brightener are fed to the crutcher. The CMC and brightener are premixed with 87 kg of the silicate and 89 kg of the water to form a slurry in which they are uniformly dispersed prior to their addition to the crutcher. The crutcher is turned on for several seconds to mix these materials; the HLAS is neutralized by the Na_2O of the silicate. The mix heats up due to the neutralization reaction; the temperature in the crutcher mix is maintained at about 75°-80°C for the remainder of the mixing operation. Temperature in the crutcher can be raised by using its steam jacket. The sulfate is added to the crutcher and it is turned on for several seconds. The ZPS is added to the crutcher and it is turned on for several seconds. The STPP is added to the crutcher and it is turned on for several seconds.

The mix is dropped out of the crutcher into a hold tank where it is mixed with several previous batches of the same components. The mix is pumped continuously from the hold tank to the spray-dryer where it is sprayed through nozzles under a pressure of about 60-70 kg/cm². The air inlet temperature of the spray-dryer is about 400°-410°C; the air outlet temperature is about 55°-60°C.

The spray-dried granules have the following composition:

Component	Percentage
NaLAS	16.75
Moisture	7.06
STPP	15.24
TSPP	3.79
Orthophosphate	0.76
Na silicate (SiO ₂ /Na ₂ O= 3.2)	7.72
A/M copolymer	0.70
CMC	0.29
DPTA	0.44
HDQA	0.73
ZPS	0.0098
Brightener	0.058
Na sulfate	45.95
Na carbonate	0.32

The TSPP and orthophosphate are present in the granules due to reversion of STPP. The carbonate is from reaction of Na₂O with CO₂ during spray-drying. The spray-dried granules have a bulk density of 417 g/l.

A finished laundry detergent product is produced by combining the above spray-dried granules with the agglomerate detergent granules from Example 3 above and the following add-on materials:

- SRA: polymeric soil release agent described hereinabove.
- Protease/amylase: protease and amylase enzyme product, trade name SAVINASE/BAN 6/100T®, from Novo Industries A/S.
- Lipase: lipase enzyme product, tradename LIPOLASE 100T®, from Novo Industries A/S.
- Cellulase: cellulase enzyme product, tradename CAREZYME 5T®, from Novo Industries A/S, activity of 5000 CEVU/g.

The following materials in the amounts indicated are fed to and mixed in a continuous tilted-drum mixer with baffles:

Material	Amount (kg/hr)
Spray-dried granules above	48.050
Agglomerates from Example 3	21.000
SRA	140
Protease/amylase	210
Lipase	56
Cellulase	70
Perfume	175
A/M copolymer (30% solution)	280
Colorant (13% aqueous solution)	75

The granules, agglomerates, and enzymes are all fed to the drum mixer as particulate solids. The perfume, A/M copolymer solution, and colorant solution are sprayed onto the dry materials near the inlet of the drum mixer.

The finished laundry detergent product contains the following:

Component	Percentage
NaLAS	18.0
Moisture	5.1
STPP	16.4
TSPP	2.9
Orthophosphate	0.6
Silicate ($\text{SiO}_2/\text{Na}_2\text{O} = 3.2$)	5.3
A/M copolymer	0.6
CMC	0.2
DPTA	0.3
HDQA	0.5
ZPS	0.007
Brightener	0.04
SRA	0.2
Protease/amylase	0.3
Lipase	0.08
Cellulase	0.1
Na sulfate	35.8
Na carbonate	13.3

The bulk density of the finished detergent product is 465 g/l.

In above Example 4, the agglomerate detergent granules of Example 1 or 2 can replace those of Example 3.

While particular embodiments of the subject invention have been described, it would be obvious to those skilled in the art that various changes and modifications to the subject invention can be made without departing from the spirit and scope of the invention. It is intended to cover, in the appended claims, all such modifications that are within the scope of this invention.

What is claimed is:

1. A continuous process for producing agglomerate detergent granules comprising the steps of:
 - (a) grinding carbonate selected from sodium carbonate, potassium carbonate, and mixtures thereof, to a freshly ground particulate carbonate having a median particle size of from about 2 to about 20 microns,
 - (b) preparing a mixture in a high-speed mixer by feeding to the mixer raw materials consisting essentially of the following:
 - (1) from about 10% to about 25% an alkylbenzene sulfonic acid;
 - (2) from about 25% to about 60% the freshly ground particulate carbonate, the amount of carbonate being at least about 10 times the amount theoretically needed to neutralize the alkylbenzene sulfonic acid;
 - (3) from about 5% to about 40% a phosphate builder selected from polyphosphates, pyrophosphates, and mixtures thereof;
 - (4) from about 5% to about 50% a sodium sulfate;
 - (5) from 0% to about 10% other surfactants;
 - (6) from 0% to about 9% water (including water in the raw materials); and
 - (7) from 0% to about 10% other materials;
 - (c) agglomerating the mixture from step (a) in a moderate-speed mixer; whereby the alkylbenzene sulfonic acid is neutralized by the carbonate and the agglomerate detergent granules are produced, and wherein the granules produced are substantially free of flow aids selected from silicas, clays, diatomaceous earth, aluminosilicates, perlite, calcite, and mixtures thereof.
2. The process according to Claim 1 wherein the high-speed mixer has a substantially cylindrical mixing chamber and a central shaft, with mixer blades attached, which rotates at a speed of from about 200 rpm to about 1800 rpm; and the moderate-speed mixer has a substantially cylindrical mixing chamber, and a central shaft, with mixer blades attached, which rotates at a speed of from about 40 rpm to about 160 rpm.

3. The process according to Claim 2 wherein the average residence time of material in the high-speed mixer is from about 2 seconds to about 30 seconds, and the average residence time of material and the moderate-speed mixer is from about 20 seconds to about 300 seconds.
4. The process according to Claim 1 wherein the freshly ground particulate carbonate has a median particle size from about 5 microns to about 15 microns, and wherein the grinding of the carbonate is less than about 48 hours prior to the feeding of the freshly ground particulate carbonate to the mixer.
5. The process according to Claim 4 wherein the carbonate is sodium carbonate, the grinding is no more than about 24 hours before the feeding, to the amount of carbonate is at least about 12 times the amount theoretically needed to neutralize the alkylbenzene sulfonic acid, the ground sodium carbonate has a median particle size of from about 5 microns to about 15 microns and a moisture content of no more than about 2%.
6. The process according to Claim 5 wherein the alkyl chain of the alkylbenzene sulfonic acid has an average of from about 11 to about 14 carbon atoms, and the phosphate builder is sodium tripolyphosphate.
7. The process according to Claim 6 wherein from about 1% to about 10% said other surfactant is fed to the process in the form of an aqueous paste comprising from about 30% to about 80% said other surfactant, and from about 20% to about 70% water.
8. The process according to Claim 6 wherein the amount of alkylbenzene sulfonic acid is from about 13% to about 22%; the amount of sodium carbonate is from about 30% to about 50%; the sodium carbonate, has a median particle size from about 8 microns to about 12 microns; the grinding is using an air-classifier mill and is no more than about 8 hours before the feeding to the mixer; the amount of sodium tripolyphosphate is from about 9% to about 30%; the amount of sodium sulfate is from about 12% to about

30%; the amount of other surfactant is from 0% to about 7%; and the amount of water is from 0% to about 6%.

9. The process according to Claim 7 wherein the raw materials comprise from about 1% to about 4% other surfactant, said other surfactant being a C₁₂-C₁₄ alkyl dimethyl hydroxyethyl quaternary ammonium cationic surfactant, said other surfactant being fed to the process as an aqueous paste comprising from about 30% to about 50% said other surfactant, and from about 50% to about 70% water.
10. The process according to Claim 7 wherein the raw materials comprise from about 3% to about 7% other surfactant, said other surfactant being a C₁₂-C₁₅ alkyl ethoxy ether sulfate surfactant having a degree of ethoxylation of from about 2 to about 5, said other surfactant being fed to the process as an aqueous paste comprising from about 50% to about 80% said other surfactant, and from about 20% to about 50% water.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 97/19165

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D17/06 C11D3/10 C11D3/06 C11D1/22 C11D11/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched (other than minimum documentation) to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P.A	US 5 573 697 A (RIDDICK, ERIC F ET AL) 12 November 1996 see column 3, line 16 - line 19 see column 3, line 33 - line 38 see column 3, line 66 - column 4, line 2 see column 2, line 28 - line 35; claims 1,8; examples 5,6; table 2	1-3
P.A	WO 97 32003 A (PROCTER & GAMBLE; ADAMS DONALD SCOTT (US); YEAZELL BURCE ALBERT (U)) 4 September 1997 see page 4, line 13 - line 28; claims; example I	1,8
A	EP 0 420 317 A (UNILEVER NV; UNILEVER PLC (GB)) 3 April 1991 see page 6, paragraph 1; claims; tables	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

30 January 1998

Date of mailing of the international search report

25/02/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2230 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl
Fax: (+31-70) 340-3016

Authorized officer

Loiselet-Taisne, S

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/19165

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5573697 A	12-11-96	WO 9638529 A	05-12-96
WO 9732003 A	04-09-97	AU 5179496 A	16-09-97
EP 0420317 A	03-04-91	CA 2026156 A,C	30-03-91
		DE 69014186 D	22-12-94
		ES 2063249 T	01-01-95
		JP 3146599 A	21-06-91
		JP 7062158 B	05-07-95
		US 5164108 A	17-11-92